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Synthesis of rare earth metal complexes incorporating amido and enolate mixed ligands: Characterization and reactivity

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ABSTRACT

The reactions of 2,6-(R)₂C₆H₃NHSiMe₃ (R = *i*Pr or Et) with excess *n*BuLi in THF or *n*-hexane, followed by treatment with LnCl₃, produced different kinds of rare earth metal complexes. Complexes incorporating amido and enolate mixed ligands having the general formula (CH₂==CHO)Ln[2,6-(*i*Pr)₂C₆H₃NSiMe₃]₂(μ -Cl)Li(THF)₃ (Ln = Y(1), Yb(2)) were prepared by the reaction of *N*-trimethylsilyl-2,6-diisopropylaniline 2,6-(*i*Pr)₂C₆H₃NSiMe₃]₂Y(THF)(μ -Cl)₂Li(THF)₂ (**3**) and {[2,6-(*E*t)₂C₆H₃NSiMe₃]₃YCl][Li(THF)₄] (**4**) were isolated when 2,6-(*E*t)₂C₆H₃NHSiMe₃ was treated with *n*BuLi in *n*-hexane, followed by treatment with 1/2 or 1/3 equiv. of YCl₃ in THF, respectively. All the structures of the complexes were determined by single-crystal X-ray analyses. Investigation on the reactivity of complexes **1** and **2** towards aromatic aldehydes in difford the disproportionation products of amides and alcohols. The reaction of the lithium amide {[2,6-(*i*Pr)₂C₆H₃(Me₃Si)N}]_Li with aromatic aldehydes in the presence of a catalytic amount of YCl₃ was also studied.

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1. Introduction

Recently, rare earth metal complexes have attracted much attention for their potential applications in catalysis [1,2]. Lanthanide complexes incorporating substituted enolate ligands of the general formula O-CR = CR'R" are generally derived from CO activation. For example, the reaction of the samarium(II) complex Cp²₂Sm(THF)₂ with 1,2-di(2-pyrdinyl)ethylene, followed by treatment with CO afforded a novel samarium(III) complex incorporating a substituted enolate ligand $Cp_2^*Sm[\mu-\eta^4-(C_5H_4N)CH=$ $C(O)C(O)=C_{H}(C_{5}H_{4}N)]SmCp_{2}^{*}$ [3]. Reaction of the samarium(II) complex Cp^{*}₂Sm(THF)₂ with CO or reaction of the samarium(II) complex Cp^{*}₂Sm(THF)₂ with unsaturated hydrocarbons followed by treatment with CO also gave novel lanthanide complexes incorporating enolate-like ligands [4,5]. More recently, Hou and his coworkers reported the reaction of CO with the tetranuclear yttrium and lutetium polyhydrido complexes $\{Cp'Ln(\mu-H)_2\}_4(THF)$ $(Cp' = C_5Me_4SiMe_3, Ln = Y, Lu)$, which leads to selective formation of ethylene and structurally characterized polyoxo and oxo/hydrido rare earth metal clusters through a proposed enolate intermediate, based on the experimental spectroscopic evidences [6]. Organolanthanide complexes having both cyclopentadienyl (Cp or MeCp) and a simple enolate ligand (O–CH=CH₂) have been reported to be prepared by the direct metallation of the organolanthanide chloride, by thermolysis of the organolanthanide alkyl complexes in THF [7a] or by thermolysis of the corresponding organolanthanide alkoxides [7b,c]. The synthesis of cyclopentadienyl-free lanthanide complexes incorporating enolate ligands is far less reported [2].

Given that the Aldol reaction goes through an enolate as an intermediate when the reaction is carried out in an inorganic base medium [8], and the lanthanide amides $[(Me_3Si)_2N]_3Ln(\mu-Cl)Li(THF)_3$ can initiate disproportionation of aromatic aldehydes to amides and alcohols [9a], and the lanthanide amides $[(Me_3Si)_2N]_3Ln$ can be the catalysts for amidation of aldehydes with amines [9b] and the Tishchenko reaction [9c] through the addition of the amido group $(Me_3Si)_2N^-$ or $(R_1R_2)N^-$ to the aldehydes, lanthanide complexes incorporating both amido and enolate ligands would possess two competitive reactive groups towards aldehydes. The reactivity of this kind of complex incorporating both amido and enolate ligands with aldehydes has scarcely been investigated.

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Recently, Steiner et al. reported that the reaction of hexaprotic phosphazene {2-(MeO)(C_6H_4NH)} $_6P_3N_3$ with excess (12 equiv.) nBuLi in THF produced a monomeric dodecanuclear complex incorporating six enolate ligands [10]. We report here the synthesis of novel lanthanide complexes incorporating amido and enolate ligands having the general formula (CH₂=CHO)Ln[2,6-(*i*Pr)₂C₆H₃NSiMe₃]₂(μ -Cl)Li(THF)₃, by the one-pot reaction of *N*-trimethylsilyl-2,6-diisopropylaniline 2,6-(*i*Pr)₂C₆H₃NHSiMe₃ with excess *n*BuLi in THF, followed by treatment with 1 equiv. of LnCl₃. The reactivity of this kind of complexes with aromatic aldehydes is also reported.

2. Results and discussion

The structurally characterized rare earth metal complexes incorporating amido and enolate mixed ligands $(CH_2 = CHO)Ln[2,6-(iPr)_2C_6H_3NSiMe_3]_2(\mu-Cl)Li(THF)_3$ (Ln = Y(1),Yb(2)) were synthesized for the first time by the one-pot reaction of N-trimethylsilyl-2,6-diisopropylaniline 2,6-(*i*Pr)₂C₆H₃NHSiMe₃ with 1.5 equiv. of *n*BuLi in THF, followed by treatment with LnCl₃ in good yields (Scheme 1). The complexes are soluble in toluene, benzene, THF and CH₂Cl₂, but only slightly soluble in *n*-hexane. These complexes were well characterized by spectroscopic methods and elemental analyses. Their structures were additionally determined by X-ray diffraction study (Figs. 1 and 2).

The ¹H NMR spectrum of complex **1** exhibited resonances at 6.90, 4.24 and 4.20 ppm, which can be attributed to the corresponding proton resonances of the enolate ligand OCH=CH₂ in the complex. The resonances of the enolate ligand exhibited coupling. The proton resonances of the enolate ligand of the complex





Fig. 1. Molecular structure of complex 1, hydrogen atoms are omitted for clarity.



Fig. 2. Molecular structure of complex 2, hydrogen atoms are omitted for clarity.

can be compared with those of the enolate ligand in $(Cp'Y)_4(OCH=CH_2)(\mu-O)(\mu-H)_5(THF)$ [6], $[(C_5H_5)_2Y(\mu-OCH=CH_2)]_2$ or $[(CH_3C_5H_4)_2Y(\mu-OCH=CH_2)]_2$ [7], and LiOCH = CH₂ [11]. Each IR spectrum of complex **1** or **2** contains a very broad strong band around 1650 cm⁻¹, which can be attributable to the C=C bond of the enolate and the phenyl ring stretch.

In order to search for the origination of the enolate ligand of the above complexes, 2,6-(Et)₂C₆H₃NHSiMe₃ was treated with *n*BuLi in *n*-hexane at first, followed by treatment with 1/2 or 1/ 3 equiv. of YCl₃ in THF respectively, and complexes with the formula $[2,6-(Et)_2C_6H_3NSiMe_3]_2Y(THF)(\mu-Cl)_2Li(THF)_2$ (3) and $\{[2,6-(Et)_2C_6H_3NSiMe_3]_3YCl\}[Li(THF)_4]$ (4) were isolated (Scheme 2). The complexes were well characterized by spectroscopic methods and elemental analyses. The elemental analyses data are in agreement with the loss of THF molecules, which is common in lanthanide chemistry. The structures of complexes 3 and 4 were determined by single crystal X-ray analyses. These results suggested that (1) the produced lithium amide $Li(2,6-(iPr)_2C_6H_3NSiMe_3)$ is not responsible for the resulting enolate ligand in complexes 1 and 2; (2) YCl₃ cannot react with THF leading to the formation of the enolate ligand. Evidence that *n*BuLi can react with THF leading to the cleavage of the THF ring to produce a lithium enolate and ethylene is reported, and this process has been monitored by NMR spectroscopy [11]. Thus, the enolate ligand in complexes 1 and **2** is believed to have come from the cleavage of the THF molecule by nBuLi. To further prove the above conclusion, the



product of the reaction of *N*-trimethylsilyl-2,6-diethylaniline with 1.5 equiv. of *n*BuLi was analyzed by ¹H NMR spectroscopy. The spectra clearly indicated the formation of Li[2,6-(Et)₂C₆H₃NSiMe₃)] and LiOCH = CH₂, and the existence of three coordinated THF molecules.

X-ray analyses confirmed that complexes **1** and **2** consisted of two amido ligands, an enolate ligand and a bridged chlorine atom connected with a lithium atom coordinated by three THF molecules. The central rare earth metal of each complex is coordinated by two nitrogen atoms of the amido ligand, an oxygen atom of the enolate ligand and a chlorine atom. The central yttrium atom in complex **3** is coordinated by two nitrogen atoms of the amido ligand, one oxygen atom of a THF molecule and two chlorine atoms (Fig. 3). The central yttrium atom in complex **4** is coordinated by three nitrogen atoms of the amido ligand and one chlorine atom



Fig. 3. Molecular structure of complex 3, hydrogen atoms are omitted for clarity.



Fig. 4. The structure of the anion in 4, hydrogen atoms are omitted for clarity.

Table 1

Selected bond distances (Å) and angles (°) for 1, 2, 3 and 4

1		2	
Y(1)-O(4)	2.103(7)	Yb(1)-O(4)	2.070(6)
Y(1)-O(4')	2.104(2)	Yb(1)–O(4')	2.067(9)
Y(1) - N(1)	2.229(5)	Yb(1)-N(1)	2.188(5)
Y(1) - N(2)	2.254(6)	Yb(1)-N(2)	2.201(5)
Y(1) - Cl(1)	2.603(2)	Yb(1)-Cl(1)	2.552(2)
Cl(1)-Li(1)	2.394(2)	Cl(1)-Li(1)	2.401(2)
Li(1) - O(1)	1.93(2)	Li(1) - O(1)	1.92(2)
Li(1)-O(2)	1.90(2)	Li(1) - O(2)	1.86(2)
Li(1)–O(3)	1.89(2)	Li(1) - O(3)	1.90(2)
C(43) - C(44)	1.351(10)	C(43) - C(44)	1.344(9)
O(4) - Y(1) - N(1)	107.1(3)	O(4) - Yb(1) - N(1)	106.1(3)
O(4) - Y(1) - N(2)	102.7(3)	O(4) - Yb(1) - N(2)	102.3(3)
N(1)-Y(1)-N(2)	126.9(2)	N(1)-Yb(1)-N(2)	127.61(2)
O(4) - Y(1) - CI(1)	105.4(3)	O(4) - Yb(1) - Cl(1)	105.2(3)
N(1)-Y(1)-Cl(1)	105.98(2)	N(2)-Yb(1)-Cl(1)	106.01(2)
N(2)-Y(1)-Cl(1)	107.08(15)	N(1)-Yb(1)-Cl(1)	107.70(2)
Li(1)-Cl(1)-Y(1)	136.3(4)	Li(1)-Cl(1)-Yb(1)	136.1(3)
3		4	
Y(1)-N(1)	2.228(3)	Y(1)-N(1)	2.302(5)
Y(1)-N(2)	2.252(4)	Y(1)-N(2)	2.292(5)
Y(1)-O(1)	2.404(3)	Y(1)-N(3)	2.289(5)
Y(1) - Cl(1)	2.657(2)	Y(1)-Cl(1)	2.621(2)
Y(1)-Cl(2)	2.638(2)	Li(1)-O(1)	1.97(2)
Cl(2)-Li(1)	2.370(2)	Li(1)-O(2)	1.95(2)
Cl(1)-Li(1)	2.331(2)	Li(1)-O(3)	1.89(2)
O(2)-Li(1)	1.90(2)	Li(1)-O(4)	1.89(2)
O(3)-Li(1)	1.92(2)	N(2)-Y(1)-N(1)	118.04(18)
N(1)-Y(1)-N(2)	120.22(14)	N(3)-Y(1)-N(1)	115.39(18)
N(1)-Y(1)-O(1)	101.27(12)	N(3)-Y(1)-N(2)	116.58(19)
N(2)-Y(1)-O(1)	92.57(13)	N(3)-Y(1)-Cl(1)	98.5(2)
N(1)-Y(1)-Cl(2)	93.10(9)	N(2)-Y(1)-Cl(1)	99.04(18)
N(2)-Y(1)-Cl(2)	91.91(10)	N(1)-Y(1)-Cl(1)	104.35(19)
O(1) - Y(1) - Cl(2)	160.16(10)		
O(1) - Y(1) - Cl(1)	80.87(10)		
N(1)-Y(1)-Cl(1)	111.46(10)		
N(2)-Y(1)-Cl(1)	128.16(11)		
Cl(2)-Y(1)-Cl(1)	81.17(5)		
Cl(1)-Li(1)-Cl(2)	94.3(4)		
O(2)-Li(1)-O(3)	105.5(5)		

(Fig. 4). The bond angles of N–Ln–N, Cl–Ln–O, N–Ln–Cl, O–Ln–N (Ln = Y, Yb), in the range 102.7(3)–126.9(2)° (Table 1) for complex **1**, 102.3(3)–127.61(19)° (Table 1) for complex **2**, and 98.5(2)–118.04(18)° for complex **4**, are deviated from the ideal tetrahedral angle. Thus the coordination geometry around the central metal of complexes **1**, **2** and **4** can be described as a distorted tetrahedral. The bond angles of O(1)–Y(1)–Cl(2), N(1)–Y(1)–N(2), N(1)–Y(1)–Cl(1) and N(2)–Y(1)–Cl(1) are 160.16(10), 120.22(14), 111.46(10) and 128.16(11)° (Table 1), respectively in complex **3**, largely deviated from the ideal trigonal bipyramidal bond angles, so the coordination geometry of the central yttrium in complex **3** can be described as pseudo-trigonal bipyramidal with O(1) and Cl(2) at the axial positions.

The Y–N distances are 2.229(5) and 2.254(6) Å, with an average of 2.242(6) Å, in **1**, which is comparable to the average distance of 2.194(5) Å found in **2**, and that of 2.240(4) Å in **3** and 2.294(5) Å in **4**, if the ionic radii difference between the central metal is taken into account. The average Y–N distance of 2.242(6) Å in **1** is similar to that of 2.243(4) Å found in $[\eta^{5}-(CH_2)_2(C_9H_6)_2]$ YN(SiMe₃)₂ [12]. But the average Yb–N bond distance of 2.194(5) Å found in **2** is slightly longer than that of 2.162(5) Å found in $[\eta^{5}-(CH_2)_2(C_9H_6)_2]$ YbN(SiMe₃)₂ [13], this difference can be attributable to ionic and steric effects [14]. The Yb–Cl distance of 2.552(2) Å found in [(Me₃Si)₂-N]₃Yb(μ -Cl)Li(THF)₃ [13a]. The Y–Cl distance of 2.603(2) Å found in **2** due to the ionic radii difference. The Y–Cl distance of 2.603(2) Å found in **2** due to the ionic radii difference. The Y–Cl distance of 2.603(2) Å found in **1** is shorter than those of 2.648(2) Å in **3** and 2.621(2) Å

in **4**, probably due to steric effects. The Ln–Cl bond distances found in the above complexes are comparable to those found in Ln{N[Si(Me)₂CH₂CH₂Si(Me)₂]}(μ -Cl)Li(L)₃ (L = THF or Et₂O) [15]. The yttrium–oxygen distance of 2.104(10) Å is shorter than those of 2.275(3) and 2.290(3) Å found in [(CH₃C₅H₄)₂Y(μ -OCH=CH₂)]₂ [7] The Li(1)–Cl(1)–Y(1) angle of 136.3(4)° in **1** is comparable to that of 136.1(3)° found in **2**, but these angles are significantly smaller than the corresponding Li–Cl–Ln angles of 175 ± 1° found in [(Me₃. Si)₂N]₃Ln(μ -Cl)Li(THF)₃ (Ln = Yb, Sm, Eu) [16], and those of 170 ± 2°

found in $Ln{N[Si(Me)_2CH_2CH_2Si(Me)_2]}(\mu-Cl)\dot{Li}(L)_3$ (L = THF or Et₂O) [15].

The C=C double bond distances of the enolate, 1.351(10) Å in **1** and 1.344(4) Å in **2**, are slightly longer than the standard 1.34 Å expected for the C=C bond in ethylene, they are also longer than that of 1.287(8) Å for the C=C double bond of the enolate found in $[(CH_3C_5H_4)_2Y(\mu-OCH=CH_2)]_2$ [7].

It has been well documented that the Aldol reaction proceeds through an enolate intermediate when the reaction is carried out in an inorganic base medium [8]. We have found that lanthanide amides $[(Me_3Si)_2N]_3Ln(\mu-Cl)Li(THF)_3$ can initiate the disproportionation reaction of aromatic aldehydes to give the corresponding amides and alcohols [9]. In order to search for the influence of the rare earth metals on the reactivity or selectivity of the amido and enolate ligands with aromatic aldehydes (Scheme 3), the reactivity of the lanthanide complexes **1** and **2** with aromatic aldehydes was explored.

First, a model reaction of 4-bromobenzyl aldehyde with a stoichiometric amount of the yttrium complex **1** was tested (Scheme 4, Table 2). It was found that the reaction can proceed in different solvents such as toluene, CH_2Cl_2 and THF (Table 2, entries 1–3), but the outputs of the reaction products are higher in CH_2Cl_2 than for reactions carried out in other solvents such as THF and toluene. It was found that only the disproportionation products of the corresponding amide and alcohol instead of the Aldol reaction product could be isolated, suggesting that the amido ligand could selectively react with aromatic aldehydes. The outputs of the reaction products were influenced by the reaction temperatures. Low yields of the products could be obtained when the reaction was carried out at moderately higher temperatures. It should be noted that a small amount of imines could be detected when the reaction was carried out at moderately higher temperatures, but the imines is

Table 2

Conditions and results of the reaction of 4-bromobenzyl aldehyde with a stoichiometric amount of yttrium complex $1^{\rm a}$

Entry	Temperature (°C)	Solvent	Time (d)	Yield of amide ^b
1	r. t.	Toluene	2	49
2	r. t.	CH_2Cl_2	2	68
3	r. t.	THF	2	35
4	50	CH_2Cl_2	2	41
5	80	THF	2	23

^a Aldehyde:yttrium complex = 4:1 (mol ratio).

^b Isolated yield based on the yttrium complex.

decomposed to aldehydes during workup. Thus, the conditions for doing the following experiments were fixed as room temperature reaction, employing CH_2Cl_2 as the solvent.

A series of aromatic aldehydes can selectively react with the amido group of the lanthanide complexes 1 and 2 to produce the corresponding disproportionation products of amides and alcohols (Scheme 5, Table 3), and no Aldol reaction products were found to any detectable degree, indicating that the electron-deficient lanthanide metal has a great influence on the reactivity of the enolate group. The substituents on the aromatic aldehydes could be either electron-donating groups such as CH₃⁻, CH₃O⁻ and Me₂N⁻ or electron-withdrawing ones such as Cl⁻, Br⁻, O₂N⁻ and F₃C⁻. However, the electronic effects of the substituent groups have an influence on the output of the reactions. When the substituents are electron-donating groups such as CH₃⁻, CH₃O⁻ and Me₂N⁻ or electron-withdrawing ones such as Cl⁻ and Br⁻, the main products of amides and alcohols (>50% yield based on the lanthanide complexes) could be isolated, and only a trace or a very small amount of the corresponding imines could be detected from the reaction mixture. When the substituents are O_2N^- and F_3C^- , the output of the imines increased as the output of the amides and alcohols decreased. The corresponding imines could be isolated under the workup conditions, and they were well characterized (Fig. 5), however, in all other cases the imine products could not be isolated under the workup conditions. These results are different to our previous work on the reaction of lanthanide amides [(Me3-Si)₂N]₃Ln(μ -Cl)Li(THF)₃ with aromatic aldehydes, producing the corresponding amides and alcohols as the only products [9a], with no imine products being found to any detectable degree.



Scheme 4.





 Table 3

 Results of the reaction of aromatic aldehydes with a stoichiometric amount of lanthanide complex 1 and 2a

Entry	Ar-	Time	Product of 5	Yield of 5 (%) ^b	Product of 6	Yield of 6 (%) ^b	Yield of product 5 '
1	$4-CH_3C_6H_4-$	2	5a	88 ^c (87) ^d	6a	85 (83)	Trace
2	4-CH ₃ OC ₆ H ₄ -	2	5b	73 (75)	6b	67 (69)	Trace
3	4-ClC ₆ H ₄ -	2	5c	74 (67)	6c	69 (65)	Trace
4	4-BrC ₆ H ₄ -	2	5d	68 (49)	6d	65 (47)	Trace
5	4-	2	5e	54 (59)	6e	51 (57)	Trace
	Me ₂ NC ₆ H ₄ -						
6	$4 - O_2 N C_6 H_4 -$	2	5f	51 (55)	6f	49 (52)	32 (39)
7	$4 - F_3 CC_6 H_4 -$	2	5g	53 (49)	6g	47 (44)	38 (37)
8	C_6H_5-	3	5h	49 (47)	6h	47 (45)	Trace

Conditions: ^aCH₂Cl₂ as a solvent, room temperature. ^bisolated yield based on lanthanide complex. ^cData are obtained from the reaction of the aldehydes with yttrium complex **1**. ^dData in the parenthesis are obtained from the reaction of the aldehydes with ytterbium complex **2**.

We have found that the reaction of lithium amide $(Me_3Si)_2NLi$ with aromatic aldehydes in the presence of $LnCl_3$, or the stoichiometric reaction of $[(Me_3Si)_2N]_3Ln(\mu-Cl)Li(THF)_3$ with aromatic aldehydes, yielded the corresponding disproportionation products of amides and alcohols. No imine product has been detected in the reaction [9a]. For comparison, the reaction of the lithium amide $\{[2,6-(iPr)_2C_6H_3](Me_3Si)N\}Li$ with some selected aromatic aldehydes catalyzed by YCl₃ was investigated (Scheme 6). The reaction goes smoothly producing the disproportionation products of amides and alcohols in the presence of 5 mol% YCl₃ (Table 4) in satisfactory yields. The substituents on the aromatic aldehydes can be either electron-donating groups such as CH_3^- and CH_3O^- or electron-withdrawing ones such as Cl^- , Br^- and O_2N^- . The major differences between the stoichiometric reactions of the lanthanide complexes 1 or 2 with aldehvdes and the catalytic reaction of lithium amide with the aldehydes are: (1) no imine products have been detected in all cases (Table 4); and (2) the output of the corresponding amides and alcohols are improved significantly when the substituents on the aromatic aldehydes are electron-withdrawing ones such as O_2N^- and F_3C^- (Table 4, entries 5 and 6) under almost the same reaction conditions. These results are somewhat different to our previous work, which may be due to the coordinated enolate ligand's effect on the reactions. We have proposed that the reaction of lithium amide (Me₃Si)₂NLi with aromatic aldehydes in the presence of LnCl₃ goes through lanthanide amides $[(Me_3Si)_2N]_3Ln(\mu-Cl)Li(THF)_3$ as intermediates. It is reported that the reaction of lithium amides {[2,6-(*i*Pr)₂C₆H₃](Me₃Si)N}Li with lanthanide chlorides LnCl₃ produced the lanthanide amides {[2,6- $(iPr)_2C_6H_3$ (Me₃Si)N₃Ln [17]. On the basis of these results, we can conclude that the reaction of lithium amide $\{[2,6-(iPr)_2C_6H_3]-$ (Me₃Si)N}Li with aldehydes in the presence of YCl₃ may go through a similar mechanism as in our previous work, which has been demonstrated as a Cannizzaro type disproportionation [9a]. The reaction involves the addition of the amido group from the lanthanide metal center to one molecule of aldehyde to give the intermediate ${ArCH(O)N(SiMe_3)[C_6H_3-2,6-(iPr)_2]}^-$ (**A**), which leads to the oxidation of the aldehyde by transferring the hydride from the intermediate (A) to another molecule of aldehyde to produce the amide precursor, leading to the reduction of the aldehyde, ArCH₂O⁻. The final products of amide and alcohols could be isolated after workup. The formation of imine products in the stoichiometric reactions of lanthanide complex 1 or 2 with aromatic aldehydes may be due to the influence of the coordinated enolate ligand in the complexes. However, further work on this detail should be carried out.



Fig. 5. Molecular structure of 5f', hydrogen atoms are omitted for clarity.



Table 4

Reaction of lithium amide {[2,6-(iPr)_2C_6H_3](Me_3Si)N}Li with aromatic aldehydes catalyzed by YCl_3^a

Entry	Ar-	Solvent	Time	Product of 5	Yield of 5 (%) ^b	Product of 6	Yield of 6 (%) ^b
1	4-CH ₃ C ₆ H ₄ -	Toluene	3	5a	76	6a	73
2	4-CH ₃ OC ₆ H ₄ -	Toluene	3	5b	70	6b	65
3	4-ClC ₆ H ₄ -	Toluene	2	5c	75	6c	74
4	4-BrC ₆ H ₄ -	Toluene	2	5d	72	6d	70
5°	$4 - O_2 N C_6 H_4 -$	CH_2Cl_2	2	5f	81	6f	75
6 ^c	$4-F_3CC_6H_4-$	CH_2Cl_2	2	5g	83	6g	79
7	C ₆ H ₅ -	Toluene	3	5h	86	6h	79

Conditions: $^{a}5$ mol% YCl_3, 80 °C; $^{b}isolated$ yield based on the lithium amide; $^{c}room$ temperature reaction.

3. Conclusion

We have for the first time rationally synthesized novel rare earth metal complexes incorporating amido and enolate mixed ligands by a one-pot reaction. The experimental results suggest that this method may be applied to the synthesis of complexes incorporating amido and enolate mixed ligands. Investigation on the reactivity of this kind of lanthanide complex indicates that the amido ligand of the complex can selectively react with aromatic aldehydes to afford the disproportionation products of amides and alcohols, suggesting that the Lewis acid property of the rare earth metals have a great influence on the reactivity of the enolate ligand. When the enolate is coordinated with the rare earth metals; it showed no reactivity with aromatic aldehydes. This kind of complex has compatibility for substituents on the aromatic aldehyde ring such as Cl^, Br^, $F_3C^-\!\!, ~O_2N^-$ and other electron-donating groups. The outputs of the reaction were influenced by the substituents on the aromatic aldehydes ring, the solvents and the ligands of the lanthanide complexes. The results of the reaction of the lithium amide $\{[2,6-(iPr)_2C_6H_3](Me_3Si)N\}$ Li with aromatic aldehydes in the presence of a catalytic amount of YCl₃ suggested that the method for the preparation of the amides from aldehydes by a one step reaction may be extended to reaction of other lithium amides with aldehydes. Further investigation on the reactivity of other lithium amides with aldehydes in the presence of lanthanide compounds is now in progress in our laboratory.

4. Experimental

4.1. Materials and methods

All syntheses and manipulations of air and moisture-sensitive materials were carried out in flamed dried Schlenk-type glassware on a Schlenk line. All solvents were refluxed and distilled over either finely divided LiAlH₄ or sodium benzophenone ketyl under argon prior to use unless otherwise noted. 2,6-(*i*Pr)₂C₆H₃NHSiMe₃ 2,6-(Et)₂C₆H₃NHSiMe₃ [17] and LnCl₃ [18] (Ln = Yb, Y) were prepared according to the literature procedures. CDCl₃ was dried over activated 4 Å molecular sieves. Elemental analysis data were obtained on a Perkin–Elmer 2400 Series II elemental analyzer. IR spectra were recorded on a BIO-RAD FTS-40 spectrometer (CsI

crystal plate, Nujol and Fluoroble mulls). Melting points were determined in sealed capillaries and are reported without correction. ¹H NMR and ¹³C NMR spectra for analyses of compounds were recorded on a Bruker Avance-300 NMR spectrometer in benzene- d_6 for the lanthanide complexes, and in CDCl₃ for organic compounds, and chemical shifts for ¹H and ¹³C NMR spectra were referenced to the internal solvent resonances.

4.2. Preparation of $(CH_2=CHO)Y[2,6-(iPr)_2C_6H_3NSiMe_3]_2(\mu-Cl)Li(THF)_3$ (1)

To a THF solution of $2,6-({}^{i}Pr)_{2}C_{6}H_{3}NHSiMe_{3}$ (5.90 g, 23.6 mmol) at $-78 \,^{\circ}\text{C}$ was slowly added an *n*-hexane solution of *n*BuLi (20.6 mL, 35.8 mmol). The temperature of the reaction mixture was then gradually raised to room temperature after the addition. The mixture was stirred at room temperature for another 12 h. The reaction mixture was then transferred to a suspension of YCl₂ (2.31 g, 11.8 mmol) in THF. The reaction mixture was stirred at room temperature for 6 h, and then at 60 °C overnight. The solvent was pumped off. The residue was washed with 15 mL of *n*-hexane. The solid was extracted with a mixture of toluene and *n*-hexane (2:3, v/v) at 50 °C. Colorless crystals were obtained upon cooling the extracts at -10 °C for several days (6.27 g, 60%). M.p.: 82-84 °C (dec.). ¹H NMR (300 MHz, C_6D_6 , δ in ppm): 7.32–7.16 (m, 6H, C_6H_3), 6.90 (dd, 1H, J = 12.9 Hz, J = 5.4 Hz, $CH = CH_2$), 4.24 (dd, 1H, J = 12.9 Hz, J = 1.2 Hz, CH=CH₂), 4.20 (dd, 1H, J = 5.4 Hz, $J = 1.2 \text{ Hz}, \text{ CH}=CH_2$), 3.12 (m, 4H, $CH(CH_3)_2$), 3.50 (m, 12H, OC₄*H*₈), 1.46 (m, 12H, OC₄*H*₈), 1.25–1.23 (m, 24H, CH(CH₃)₂), 0.50 (s, 18H, Si(CH₃)₃). IR (Nujol and Fluoroble mulls, cm⁻¹): v 2961 (w), 2870 (s), 1651 (vs), 1441 (m), 1383 (m), 1327 (w), 1252 (vs), 1196 (w), 1044 (w), 907 (s), 843(s). Anal. Calc. for C₄₄H₇₉ClLiN₂O₄₋ Si₂Y: C, 59.54; H, 8.97; N, 3.16. Found: C, 59.26; H, 9.13; N, 3.00%.

4.3. Preparation of (CH₂=CHO)Yb[2,6-(iPr)₂C₆H₃NSiMe₃]₂(μ-Cl)Li(THF)₃ (**2**)

This complex was prepared as yellow crystals in 61% yield from the reaction of 2,6-(*i*Pr)₂C₆H₃NHSiMe₃ (4.45 g, 17.8 mmol) with *n*BuLi (15.5 mL, 26.9 mmol) in THF, followed by treatment with YbCl₃ (2.49 g, 8.9 mmol) by applying the procedures similar to those used for the preparation of **1**. M.p.: 86–88 °C (dec.). IR (Nujol and Fluoroble mulls, cm⁻¹): 2960 (s), 2870 (w), 1632 (vs), 1462 (m), 1363 (m), 1263 (w), 1092 (w), 1057 (w), 745 (w). *Anal.* Calc. for C₄₄H₇₉ClLiN₂O₄Si₂Yb (971.70): C, 54.39; H, 8.19; N, 2.88. Found: C, 54.12; H, 8.03; N, 2.98%.

4.4. Preparation of $[2,6-(Et)_2C_6H_3NSiMe_3]_2Y(THF)(\mu-Cl)_2Li(THF)_2$ (3)

To a Schlenk flask containing an *n*-hexane solution of 2,6-(Et)₂C₆H₃NHSiMe₃ (2.78 g, 12.6 mmol) was added *n*BuLi (10.6 mL, 13.0 mmol) at -78 °C. The reaction mixture temperature was slowly raised to room temperature, and it was stirred for another 12 h at room temperature. The excess nBuLi was filtered off and washed with n-hexane, then 30 mL of THF was added. To the THF solution of the resulting lithium amide Li[2,6-(Et)₂C₆H₃NSiMe₃], was added YCl₃ (1.23 g, 6.3 mmol). The reaction mixture was stirred at room temperature overnight, and then at 60 °C for another 24 h. The solvent was evaporated under reduced pressure. The residue was extracted with toluene and *n*-hexane mixed solvents (1:1, v/v, 2 × 10 mL), the extraction was combined and concentrated. Colorless crystals were obtained upon standing the concentrated solution at -20 °C for several days (3.54 g, 83%). M.p.: 86–88 °C. ¹H NMR (300 MHz, C_6D_6 , δ in ppm): 7.20–6.94 (m, 6H), 3.37-3.26 (m, 4H), 2.97-2.88 (m, 8H), 1.46-1.33 (m, 4H), 1.24–1.19 (m, 12H), 0.46–0.34 (m, 18H). IR (KBr, cm⁻¹): 3406 (w), 2966 (s), 2874 (w), 1624 (s), 1454 (s), 1253 (vs), 1107

(m), 1060 (w), 902 (m), 840 (w), 748 (w). Anal. Calc. for $C_{30}H_{52}Cl_2LiN_2OSi_2Y$ (**3**-2THF) (679.67): C, 53.01; H, 7.71; N, 4.12. Found C, 52.81; H, 7.36; N, 3.75%.

4.5. Preparation of $\{[2,6-(Et)_2C_6H_3NSiMe_3]_3YCl\}[Li(THF)_4]$ (4)

This complex was prepared as colorless crystals in 75% yield from the reaction of 2,6-(Et)₂C₆H₃NHSiMe₃ (4.59 g, 20.8 mmol) with *n*BuLi (17.4 mL, 21.4 mmol) in *n*-hexane, followed by treatment with YCl₃ (1.35 g, 6.9 mmol) in THF, by employing procedures similar to those used for the preparation of complex **3**. ¹H NMR (300 MHz, C₆D₆, δ in ppm): 7.19–6.92 (m, 6H), 3.35–3.25 (m, 4H), 2.95–2.88 (m, 8H), 1.45–1.30 (m, 4H), 1.24–1.19 (m, 12H), 0.46–0.34 (m, 18H). IR (KBr, cm⁻¹): 2962 (s), 2874 (m), 2330 (w), 1631 (s), 1454 (s), 1373 (w), 1253 (vs), 1111 (s), 1057 (m), 906 (s), 840 (m), 748 (w). *Anal.* Calc. for C₄₃H₇₄ClLiN₃OSi₃Y (**4**-3THF) (864.62): C, 59.73; H, 8.63; N, 4.86. Found: C, 59.49; H, 8.63; N 4.97%.

4.6. Reaction of N-trimethylsilyl-2, 6-diethylaniline with nBuLi

To a Schlenk flask containing a tetrahydrofuran (THF) solution of 2,6-(Et)₂C₆H₃NHSiMe₃ (0.278 g, 1.26 mmol) was added *n*BuLi (1.60 mL, 2.0 mmol) at -78 °C. The reaction mixture temperature was slowly raised to room temperature after the addition, and it was stirred for another 12 h at room temperature. The excess *n*BuLi was filtered off and washed with *n*-hexane. The solvents were pumped off, and the solid product was dried under vacuum. ¹H NMR (300 MHz, C₆D₆, δ in ppm): 7.08–7.06 (m, 6 H), 6.69 (dd, 1H, *J* = 12.5 Hz, *J* = 6.9 Hz, *CH*=CH₂), 3.99 (dd, 1H, *J* = 12.5 Hz, *J* = 1.2 Hz, CH=CH₂), 3.72 (dd, 1H, *J* = 6.9 Hz, *J* = 1.2 Hz, CH=CH₂), 3.43 (m, 12H, OC₄H₈), 2.94 (t, 8H, *J* = 7.2 Hz, CH₂CH₃), 1.45 (m, 12H, OC₄H₈), 1.32 (t, *J* = 7.2 Hz, 12H, CH₂CH₃), 0.24 (s, 18H, Si(CH₃)₃). This clearly shows the formation of Li[2, 6-(Et)₂C₆H₃NSiMe₃], LiOCH = CH₂ and the existence of three coordinated THF molecules.

4.7. Reaction of complexes 1 or 2 with aromatic aldehydes

A 30 mL Schlenk tube was charged with the complex (1 mmol) under dried argon. To the flask were added CH_2Cl_2 (3 mL) and the aromatic aldehydes (4 mmol). The reaction mixture was stirred at room temperature for 2–3 days; the mixture was then quenched with diluted HCl (0.1 M, 1.0 mL). The mixture was extracted with acetyl acetate, and the extracts were dried over MgSO₄ and filtered. The solvent was removed by rotary evaporation. The residue was purified with a flash chromatography column (10:1 *n*-hexane:acetyl acetate, v/v) to give the corresponding products. In the case of the reactions of aromatic aldehydes having strong electron-withdrawing groups, such as O_2N^- and F_3C^- , with stoichiometric amounts of complexes **1** or **2**, the imine products could be isolated and characterized under the experimental conditions.

4.8. Reaction of lithium amide $\{[2,6-(iPr)_2C_6H_3](Me_3Si)N\}Li$ with aromatic aldehydes catalyzed by YCl_3

A 30 mL Schlenk tube was charged with YCl₃ (5 mol%). To the tube were added solvent (toluene, or CH₂Cl₂, 3 mL), lithium amide [2,6-(*i*Pr)₂C₆H₃NSiMe₃]Li (1 mmol) and the aromatic aldehyde (2 mmol). The reaction mixture was stirred at a certain temperature for a fixed interval; the mixture was then quenched with diluted HCl (0.1 M, 1.0 mL). The mixture was extracted with acetyl acetate, and the extracts were dried over MgSO₄ and filtered. The solvent was removed by rotary evaporation. The residue was purified with flash chromatography column (10:1 *n*-hexane:acetyl acetate, v/v) to give the corresponding products.

4.9. X-ray crystallography

A suitable crystal of each of the complexes **1**, **2**, **3**, **4** and **5f**' was mounted in a sealed capillary. Diffraction was performed on a Siemens SMART CCD-area detector diffractometer using graphitemonochromated Mo K α radiation (λ = 0.71073 Å); temperature

Table 5

Crystallographic data and	structure refinement de	etails for 1 , 2 , 3 ,	4 and and 5
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	1	2	3	4	5f′
Empirical formula	C44H79CILiN2O4Si2A	C44H79CILiN2O4Si2Ap	C38H68Cl2LiN2O3Si2A	C55H98ClLiN3O4Si3A	C ₁₉ H ₂₂ N ₂ O ₂
Formula weight	887.57	971.70	823.87	1080.93	310.39
Crystal system	triclinic	triclinic	orthorhombic	monoclinic	monoclinic
Space group	ΡĪ	ΡĪ	Pna2 ₁	$P2_1/n$	P2 ₁ /c
a (Å)	13.123(2)	13.041(2)	37.272(2)	18.494(2)	8.4963(2)
b (Å)	13.266(2)	13.246(2)	12.2901(8)	17.872(2)	28.2166(7)
c (Å)	16.606(3)	16.579(3)	10.0790(7)	19.879(3)	8.1526(2)
α (°)	85.256(3)	85.127(2)	90	90	90
β(°)	84.929(3)	84.736(3)	90	97.657(2)	117.122(2)
γ (°)	66.722(3)	66.766(2)	90	90	90
V (Å ³)	2641.7(7)	2616.7(7)	4617.0(5)	6511.9(14)	1739.56(7)
T (K)	294(2)	294(2)	293(2)	293(2)	293(2)
$\rho_{\text{calc.}}(\text{g/cm}^3)$	1.116	1.233	1.175	1.103	1.185
Ζ	2	2	4	4	4
F(000)	952	1014	1724	2328	664
Reflections collected	13552	13397	38934	55 588	9238
Unique reflections	9282	9185	9993	15001	3051
R _{int}	0.056	0.036	0.050	0.111	0.031
Parameters refined	538	538	453	629	213
λ (Å); Μο Κα	0.71073	0.71073	0.71073	0.71073	0.71073
$\mu (\mathrm{mm}^{-1})$	1.236	1.920	1.463	1.032	0.077
θ Range (°)	1.67-25.02	1.68-25.02	1.74-27.52	1.41-27.60	1.44-25.00
Goodness-of-fit (GOF) on F^2	0.984	1.027	1.016	0.960	1.031
$R\left[I > 2\sigma(I)\right]$	0.070	0.053	0.053	0.088	0.045
wR ₂ (all data)	0.229	0.138	0.143	0.318	0.121
Largest difference in peak and hole (e $Å^{-3}$)	0.459 and -0.377	1.875 and -1.763	0.401 and -0.335	2.433 and -1.502	0.142 and -0.135

294(2) K; ψ and ω scan technique; sadabs effects and empirical absorption were applied in the data corrections. All the structures were solved by direct methods (SHELXS-97) [19], completed by subsequent difference Fourier syntheses and refined by full-matrix least-square calculations based on F^2 (SHELXS-97) [19]. See Table 5 for crystallographic data.

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Appendix A. Supplementary data

CCDC 684085, 684086, 684087, 684088 and 684089 contain the supplementary crystallographic data for 1, 2, 3, 4 and 5f'. These data can be obtained free of charge via www.ccdc.ac.uk/conts/ retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.05.030.

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